



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Europium complexes with high total photoluminescence quantum yields in solution and in PMMA

Citation for published version:

Moudam, O, Rowan, BC, Alamiry, M, Richardson, P, Richards, BS, Jones, AC & Robertson, N 2009, 'Europium complexes with high total photoluminescence quantum yields in solution and in PMMA', *Chemical Communications*, vol. 2009, no. 43, pp. 6649-6651. <https://doi.org/10.1039/b914978c>

Digital Object Identifier (DOI):

[10.1039/b914978c](https://doi.org/10.1039/b914978c)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Peer reviewed version

Published In:

Chemical Communications

Publisher Rights Statement:

Copyright © 2009 by the Royal Society of Chemistry. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Post-print of a peer-reviewed article published by the Royal Society of Chemistry.

Published article available at: <http://dx.doi.org/10.1039/B914978C>

Cite as:

Moudam, O., Rowan, B. C., Alamiry, M., Richardson, P., Richards, B. S., Jones, A. C., & Robertson, N. (2009). Europium complexes with high total photoluminescence quantum yields in solution and in PMMA. *Chemical Communications*, 2009(43), 6649-6651.

Manuscript received: 23/07/2009; Accepted: 09/09/2009; Article published: 25/09/2009

Europium Complexes with High Total Photoluminescence Quantum Yields in Solution and in PMMA**

Omar Moudam,¹ Brenda. C. Rowan,² Mohammed Alamiry,¹ Patricia Richardson,¹
Bryce. S. Richards,² Anita. C. Jones,¹ and Neil Robertson,^{1,*}

^[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

^[2]Heriot-Watt University, School of Engineering and Physical Sciences, Edinburgh, UK.

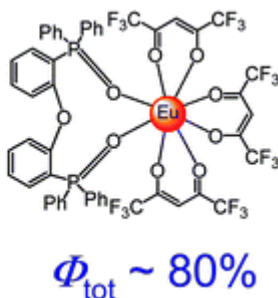
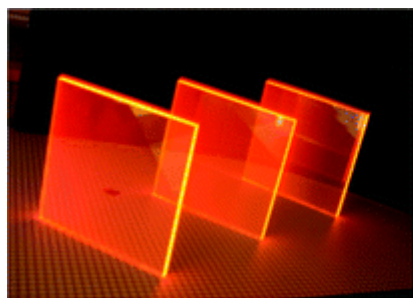
^[*]Corresponding author; e-mail: neil.robertson@ed.ac.uk, fax: +44 (0)1316504743, tel: +44 (0)1316504755

^[**]We thank the EPSRC (Grant EP/F02732X) for financial support and Simon Fitzgerald of Horiba Jobin Yvon for technical advice on use of the integrating sphere.

Supporting information:

†Electronic Supplementary Information (ESI) available: Instrumental and experimental procedures; synthesis and full characterization of **1** – **5**; Partial X-ray structural description for **4**; emission spectra of **3** – **5** in DCM and PMMA; excitation spectra **3** – **5** in DCM; absorption spectrum of **3** in DCM; decay data for **5** in PMMA. See <http://dx.doi.org/10.1039/B914978C>

Graphical abstract:



Abstract

We have prepared complexes of formula $[\text{Eu}(\text{beta-diketonate})_3(\text{DPEPO})]$ and shown quantitative excited-state energy transfer from the ligands combined with efficient Ln luminescence leading to exceptionally-high total photoluminescence quantum yield of up to 80% in solution and in PMMA.

Introduction

Lanthanide (Ln) ions have important technological uses in optical,¹ optoelectronic,² supramolecular,³ biological labeling⁴ and sensing⁵ applications due to their intense, narrow emission bands that show little dependence on the coordinated ligands. Typically, however, they exhibit low absorption coefficients and require sensitization with highly-absorbing antenna ligands to effectively utilize their luminescence properties. The intramolecular transfer of optical excitation energy from organic ligands results in emission bands due to electronic transitions between the 4f energy levels of the lanthanide. Such Ln complexes display large Stokes shifts (>150 nm) and long luminescence lifetimes in the millisecond range.⁶ Eu(III) has attracted particular attention, because of its intense red emission dominated by a narrow band at around 614 nm.³

Luminescent dyes are important in areas such as energy conversion, with functions such as frequency downshifting,⁷ light-harvesting and light-concentration in luminescent solar concentrators.⁸ For such applications, efficient photoluminescence in a solid matrix, combined with the typically large Stokes shift displayed by lanthanide complexes, are essential characteristics.⁹ The total photoluminescence quantum yield upon photoexcitation of the ligand (Φ_{tot}) is the product of the efficiency of ligand sensitization (η_{sens}) and the intrinsic luminescence efficiency of the Ln ion (Φ_{Ln}). Despite the technological importance of maximizing Φ_{tot} , the majority of studies in polymer hosts to date report only Φ_{Ln} derived from luminescence lifetime measurements^{10,11} or by direct excitation of the lanthanide.¹²

In this work, we report the synthesis and photophysical properties of three new Eu(III) complexes displaying Φ_{tot} of up to 0.76 in solution and comparable values in polymethylmethacrylate (PMMA), a common, low-cost, simply-prepared polymer of excellent optical quality. To the best of our knowledge, such high Φ_{tot} in PMMA is unprecedented. The new Eu(III) complexes (Figure 1) are of structure $[\text{EuL}_3(\text{DPEPO})]$, where DPEPO = bis(2-(diphenylphosphino)phenyl)ether oxide, L = hexafluoroacetylacetonate (hfac) **3**, tetradecafluorononadione (tfn) **4** and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (dho) **5**. DPEPO was previously used by Xu *et al*¹³ who observed efficient energy transfer to the Eu ion in a dye studied as an OLED emitter. Thus in our work, DPEPO combined with fluorinated β -diketonates is an excellent choice to maximise photoluminescence efficiency of Eu complexes applied instead to polymer films. For comparison, we also report our photophysical data for two known complexes, $[\text{Eu}(\text{hfac})_3(\text{H}_2\text{O})_2]$ **1** and $[\text{Eu}(\text{hfac})_3(\text{phen})]$ **2**, phen = 1,10-phenanthroline.

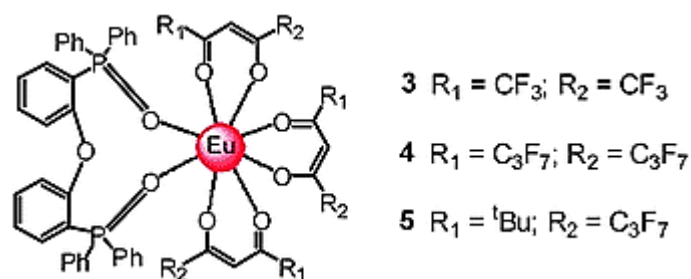


Figure 1. Molecular structure of complexes **3** [Eu(hfac)₃(DPEPO)], **4** [Eu(tfn)₃(DPEPO)] and **5** [Eu(dho)₃(DPEPO)]

Each complex has been fully characterised by NMR, CHN analysis and mass spectrometry.

Luminescence spectra (supporting information), lifetimes, τ_{Ln} , (see supporting information for typical decay data) and total quantum yields, Φ_{tot} , were measured for each complex both in dichloromethane (DCM) solution and encapsulated in a PMMA matrix, using a Horiba-Jobin-Yvon Fluoromax-P spectrometer. Total quantum yields were determined by absolute measurement, using a Horiba-Jobin-Yvon integrating sphere.¹⁴

The intrinsic quantum yields, Φ_{Ln} , were calculated from the ratio of the lanthanide luminescence lifetime, τ_{Ln} , and its pure radiative lifetime, τ_R . The latter was determined from the corrected emission spectrum, according to the method described by Werts *et al.*¹⁵ The values of the luminescence and radiative lifetimes and the intrinsic and total quantum yields are given in Table 1. Each complex shows a UV excitation band between 250 and 350 nm (supporting information), consistent with absorption by the β -diketonate and/or DPEPO ligands, and the typical $^5D_0 \rightarrow ^7F_J$ emission peaks of Eu^{3+} at 578, 592, 613, 650 and 697 nm.¹⁴

	1	2	3	4	5
DCM					
τ_{Ln} / ms	0.65	0.87	0.86	0.83	0.89
τ_R / ms	1.07	1.16	1.11	1.01	1.11
Φ_{Ln}	0.61	0.75	0.78	0.81	0.80
Φ_{tot}	0.32	0.44	0.76	0.70	0.34
η_{sens}	0.52	0.59	0.97	0.86	0.43
PMMA					
τ_{Ln} / ms	0.42	0.51	0.77	0.75	0.78
τ_R / ms	1.45	1.33	0.96	0.99	1.10
Φ_{Ln}	0.29	0.38	0.80	0.75	0.71
Φ_{tot}	0.26	0.36	0.85	0.73	–
η_{sens}	0.90	0.95	1.0	1.0	–

^a Footnote text.

Table 1. Photophysical properties of **1** – **5**. The estimated errors in Φ_{tot} and Φ_{Ln} values are $\pm 10\%$ and $\pm 5\%$, respectively. Φ_{tot} could not be determined for **5** in PMMA.[‡]

All five complexes show excellent values of Φ_{Ln} in DCM, ranging from 0.61 to 0.81, which are at the upper end of literature values for related complexes^{16, 17} and for **3–5** approach the record solution-phase value of 0.92 reported for a Eu complex with (undeuterated) β -diketonate and trioctylphosphineoxide ligands.¹⁸ It is evident that an enhancement of Φ_{Ln} is achieved through use of the DPEPO ligand in **3 – 5**. The only previously known DPEPO complex of form [Eu(β -diketonate)₃(DPEPO)] was reported by Xu *et al*, with R₁ = CF₃; R₂ = 2-thiophene (TTA) and displayed Φ_{tot} = 0.55,¹³ with the favorable properties of DPEPO attributed to a more rigid and compact structure that can reduce relaxation of the excited state. In comparison with solution studies, far fewer studies of Eu emission have been carried out in PMMA.^{1,19,20,21} Strikingly, our work shows the role of DPEPO is much more significant in PMMA than in DCM, with **3 – 5** displaying markedly higher Φ_{Ln} than **1** and **2** in the polymer matrix and with the combination of DPEPO and hfac ligands (**3**) appearing optimal, giving a value of 0.8. This may arise from enhanced encapsulation of the Eu centre that reduces the detrimental effect of C-H oscillators in the PMMA matrix that provide non-radiative decay pathways for the Eu excited state. High reported Φ_{Ln} values of Eu complexes in PMMA or other polymers are very rare and involve ligand fluorination/deuteration¹² or comparatively expensive fluorinated polymers.²¹

In determining the potential value of emissive Eu complexes in optical applications, such as frequency downshifting and light concentration, Φ_{tot} is the term of practical importance. Thus, it is essential to achieve high sensitization efficiency, η_{sens} , as well as high Φ_{Ln} , although studies of Eu complexes in polymer hosts typically determine Φ_{Ln} , only. For **3** and **4**, in both DCM and PMMA, the efficiency of energy transfer from the excited ligands to the Eu(III) is around 100%, leading to exceptionally high values of Φ_{tot} . For **1**, **2** and **5** in DCM, sensitization is much less efficient. The absence of detectable ligand fluorescence from any of the complexes, in DCM or PMMA, demonstrates efficient intersystem crossing followed by energy transfer from the ligand triplet state, with η_{sens} being determined by the competition between energy transfer and other non-radiative decay channels of the triplet state. For **1** and **2**, the substantial increase in η_{sens} on going from DCM to PMMA is consistent with the elimination of collisional quenching of the ligand triplet state in the polymer matrix. Comparison of **1** and **3** shows that the presence of the DPEPO ligand almost doubles the sensitization efficiency, at the excitation wavelength (340 nm) at which Φ_{tot} was measured. This indicates that the efficiency of energy transfer from DPEPO to Eu³⁺ is greater than that from hfac and suggests that DPEPO is predominantly excited at 340 nm. It is also notable that the excitation spectrum of **3** is essentially identical to the absorption spectrum (supporting information), indicating that the sensitization efficiency is close to unity across the entire absorption envelope. Thus, in **3**, the sensitization efficiency via excitation of hfac is substantially enhanced relative to **1**. This can be accounted for by the occurrence of efficient energy transfer from the excited hfac ligand to DPEPO, followed by efficient energy transfer from DPEPO to Eu³⁺. Importantly, this differs from the work of Xu *et al* where energy transfer to Eu was suggested to occur from the TTA ligand whose first triplet excited state lies lower than that of DPEPO. The high Φ_{tot} we observe for **3** in PMMA is strikingly illustrated (Fig. 2) by UV irradiation of the surface of a PMMA sheet containing this

complex. This leads to wave-guiding of emitted red light to the edge of the sheet where its intensity is highly concentrated.

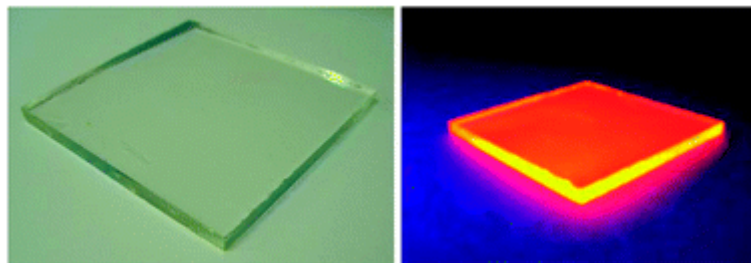


Figure 2. PMMA sheet containing **3** without (left) and with (right) UV irradiation from above. Wave-guiding of the emitted light to the sheet edge through total internal reflection is apparent.

In summary, we have demonstrated exceptionally high values of total photoluminescence quantum yield (Φ_{tot}) of Eu(III) complexes in solution and in the common optical polymer PMMA. The latter we believe to be the highest reported values, crucial for the realization of optical applications that exploit the unique photophysical characteristics of Eu(III), such as the visible red emission, large Stokes shift and spectral purity.

Notes and references

‡ Φ_{tot} of **5** in PMMA could not be measured because the complex was unstable to incorporation in the polymer matrix and the absorbance due to intact complexes (rather than partially or fully dissociated species) could not be quantified.

- [1] S. Moynihan, R. Van Deun, K. Binnemans, J. Krueger, G. von Papen, A. Kewell, G. Crean, G. Redmond, *Optical Materials*, 2007, **29**, 1798.
- [2] A. de Bettencourt-Dias, *Dalton Trans.*, **2007**, 2229.
- [3] N. Sabbatini, M. Guardigli, J-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201.
- [4] A. Dossing, *Eur. J. Inorg. Chem.*, **2005**, 1425.
- [5] S. Pandya, J. Yu, D. Parker, *Dalton Trans.*, **2006**, 2757.
- [6] Y. Yang, J. Li, X. Liu, S. Zhang, K. Driesen, P. Nockemann, K. Binnemans, *ChemPhysChem*. 2008, **9**, 600.
- [7] E. K. Klampaftis, D. Ross, B. S. Richards, *Solar Energy Materials and Solar Cells* (in press); K. R. McIntosh, G. Lau, J. N. Cotsell, K. Hanton, D. L. Bätzner, F. Bettiol, B. S. Richards, *Progress in Photovoltaics* (in press, DOI: 10.1002/pip.867).
- [8] B. Rowan, B. S. Richards, N. Robertson, A. C. Jones, P. Richardson, O. Moudam, 23rd European Photovoltaic Conference, 2008, 1 – 5 Sep, Valencia, Spain; R. Reisfeld, *Inorg. Chim. Acta.*; 1987, **140**, 345; B. C.
- [9] Rowan, L. R. Wilson, B. S. Richards, *IEEE Journal of Selected Topics in Quantum Electronics* 2008, **14**, 1312.
- [10] R. W. Olsen, R. F. Loring, M. D. Fayer, *Applied Optics*, 1981, **20**, 2934.
- [11] J. Kai, D. F. Parra, H. F. Brito, *J. Mater. Chem.*, 2008, **18**, 4549; D. F. Parra, H. F. Brito, J. D. R. Matos, L. C. Dias, *J. Appl. Polymer Sci.*, 2002, **83**, 2716.
- [12] B. Yan, X-F. Qiao, *J. Phys. Chem. B*, 2007, **111**, 12362.
- [13] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, *J. Chem. Phys. A.*, 2003, **107**, 1697.

- [14] H. Xu, L-H. Wang, X-H. Zhu, K. Yin, G-Y. Zhong, X-Y. Hou, W. Huang, *J. Phys. Chem. B.*, 2006, **110**, 3023.
- [15] L. R. Wilson, B. S. Richards, *Applied Optics*, 2009, **48**, 212.
- [16] M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem, Chem. Phys.*, 2002, **4**, 1542.
- [17] C. R. De Silva, J. R. Maeyer, R. Wang, G. S. Nichol, Z. Zheng, *Inorg. Chim. Acta.*, 2007, **360**, 3543.
- [18] S. Biju, D. B. Ambili, M. L. P. Reddy, B. M. Kariuki, *Inorg. Chem.*, 2006, **45**, 10651.
- [19] R. Pavithran, N. S. S. Kumar, S. Biju, M. L. P. Reddy, S. A. Junior, R. O. Freire, *Inorg. Chem.*, 2006, **45**, 2184.
- [20] J. J. Ding, H. F. Jiu, J. Bao, J. C. Lu, W. R. Gui, Q. J. Zhang, C. Gao, *J. Comb. Chem.*, 2005, **7**, 69
- [21] H-G. Liu, Y-I. Lee, S. Park, K. Jang, S. S. Kim, *J. Luminescence*, 2004, **110**, 11.
- [22] Y. Hasegawa, K. Sogabe, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, *Chem. Lett.* **1999**, 35.